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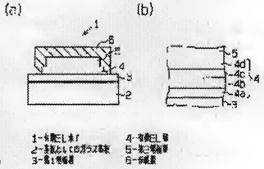
(54) ORGANIC ELECTROLUMINESCENT ELEMENT AND ITS MANUFACTURING METHOD

(57)Abstract:

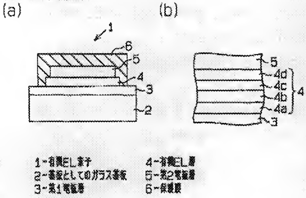
PROBLEM TO BE SOLVED: To provide an organic electroluminescent (EL) element equipped with a protective film of a simple structure and a superb adhesiveness to a layer to be coated, having flexibility even if it is thickened for securing gas barrier property and durability needed.

SOLUTION: The organic EL element 1 has a first electrode layer (a positive electrode) 3, an organic EL layer 4, and a second electrode layer (a negative electrode) 5 laminated in turn on the surface of a glass substrate 2. A protective film 6 is formed so as to coat a whole of the organic EL layer 4 and the second electrode layer 5 and a part of the first electrode layer 3. The protective layer 6 is formed of a diamond-like carbon film containing silicon. Content of silicon is preferably 2 to 20 at.%.

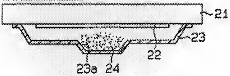


DRAWINGS

[Drawing 1]



[Drawing 2]



[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1]It is a mimetic diagram in which (a) shows the type section figure of the organic EL device of 1 embodiment, and (b) shows the details of an organic electroluminescence layer.
[Drawing 2]The mimetic diagram of the organic EL device of conventional technology.
[Description of Notations]
1 [-- An organic electroluminescence layer, 5 / -- The 2nd electrode layer, 6 / -- Protective film.] -- An organic EL device, 2 -- The glass substrate as a substrate, 3 -- The 1st electrode layer, 4

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to an organic electroluminescence (only henceforth organic electroluminescence) element, and a manufacturing method for the same, and relates to an organic EL device provided with the protective film in detail, and a manufacturing method for the same.
[0002]
[Description of the Prior Art]As for the organic EL device, the organic electroluminescence layer is formed between the 1st electrode (anode) and the 2nd electrode (negative pole). Since organic electroluminescence material has high reactivity with oxygen and moisture, if it is not used in the state where it was intercepted from the open air, chemicals degradation arises with oxygen and the moisture in the atmosphere, and there is a problem that the field which is called a dark spot and which does not emit light spreads. As a method of intercepting an organic electroluminescence layer from the open air, what is put in practical use is only a thing of composition of accommodating and closing adsorbent in covering while providing covering made from stainless steel. As this thing is shown in drawing 2, the organic electroluminescence layer 22 was formed in the rear face (undersurface) of the glass substrate 21, and the covering 23 made from stainless steel has pasted up that organic electroluminescence layer 22 on the glass substrate 21 in the wrap state. The adsorbent (drier) 24 is accommodated in the seat part 23a in the covering 23. The electrode layer is provided so that the organic electroluminescence layer 22 may be inserted, but the electrode layer is omitting the graphic display.
[0003]The method of covering an organic electroluminescence layer by a protective film is also proposed. For example, to JP,10-261487,A. In the organic EL device with which the organic layer was laminated between the hole injection electrode and the electron injection electrode, the organic EL device which provided the protective film for antioxidizing of the organic EL device which becomes a field by the side of an electron injection electrode from a diamond Mr. carbon (DLC: diamond like carbon) film is proposed at least.
[0004]By manufacturing the protective film of an organic EL device by a method including following (a) and (b)2 process, even if thickness is thin, the method of forming the protective film which can control that moisture and oxygen penetrate to an organic electroluminescence layer by high density is proposed

by JP,2000-133440,A.

(a) The process of forming the 1st DLC layer stuck to the ground film formed in the substrate by predetermined hydrogen content pressing down to which internal stress becomes small. (b) The process of forming the hydrogen which becomes large [density] about the 2nd DLC layer under the conditions which are not included substantially on the 1st DLC layer.

[0005]

[Problem(s) to be Solved by the Invention]However, in the composition which uses the covering 23 made from stainless steel put in practical use, it is disadvantageous in respect of slimming down of a material cost, a production man hour, and an element, etc. It is necessary to accommodate adsorbent, such as BaO. There is a problem of being inapplicable to a flexible substrate.

[0006]The protective film which, on the other hand, has sufficient performance which is dramatically severe as for required gas barrier property and endurance, and does not give a damage to an organic electroluminescence layer although it is advantageous in respect of cost, a man day, and slimming down with the composition which covers a protective film on the outside of an organic EL device has not reached a utilization level yet.

[0007]Like the method indicated by JP,10-261487,A, when a protective film is constituted from a DLC film, adhesion is insufficient, In order to secure required gas barrier property, when thickness is thickened, internal stress becomes large and there is a problem that flexibility required for a crack and exfoliation to occur or apply to a flexible substrate is hard to be obtained.

[0008]In order to form the protective film indicated by JP,2000-133440,A, while it becomes indispensable [a foundation layer] while forming the DLC film more than two-layer [from which manufacturing conditions differ at least], and a manufacturing process becomes complicated, there is a problem that productivity is also low.

[0009]This invention is made in view of said conventional problem, and the purpose has the good adhesion over the layer which should be covered with an easy structure, In order to secure required gas barrier property and endurance, even if it thickens thickness, it is in providing the organic EL device provided with the protective film which has flexibility applicable to a flexible substrate. The 2nd purpose is to provide the manufacturing method.

[0010]

[Means for Solving the Problem]In order to attain said 1st purpose, in the invention according to claim 1, a protective film which consists of a diamond like carbon film which contains silicon on the surface of an organic electroluminescence element was formed.

[0011]As compared with the usual DLC film which does not contain silicon by constituting a protective film from this invention with a DLC film containing silicon, adhesion is good, and in order to secure barrier property to the open air containing oxygen and moisture, even if it carries out high speed film formation of the thick film, it can control that internal stress becomes large. Also when a flexible substrate is used as a substrate, bending of a substrate can be followed and it can bend.

[0012]setting to the invention according to claim 1 in the invention according to claim 2 -- said protective film -- silicon -- 2 - 20at% -- it contains. In this invention, the aforementioned effect becomes high. In order to attain the 2nd purpose in the invention according to claim 3. On a substrate, after laminating the

1st electrode layer, an organic electroluminescence layer, and the 2nd electrode layer, a diamond like carbon film containing silicon is formed with plasma CVD method etc. so that said organic electroluminescence layer and the whole 2nd electrode layer may be covered at least.

[0013]In this invention, after being formed so that the 1st electrode layer, an organic electroluminescence layer, and the 2nd electrode layer may be laminated in order on a substrate, a protective film which consists of a DLC film containing silicon is formed so that the whole exposed surface of said organic electroluminescence layer and the 2nd electrode layer may be covered at least. Since a DLC film containing silicon is formed by a plasma-CVD (Chemical Vapor Deposition) method etc. like the usual DLC film, it can use the usual plasma CVD method.

[0014]

[Embodiment of the Invention]Hereafter, the 1 embodiment which materialized this invention is described according to drawing 1. Drawing 1 (a) is the type section figure which fractured the protective film portion of the organic EL device, and drawing 1 (b) is a mimetic diagram showing the composition of an organic electroluminescence layer. As shown in drawing 1 (a), the organic EL device 1 is laminated by the surface of the glass substrate 2 as a substrate in order of the 1st electrode layer (anode) 3, the organic electroluminescence layer 4, and the 2nd electrode layer (negative pole) 5, for example. And the protective film 6 (sealing film) is formed so that the organic electroluminescence layer 4 and 2nd electrode layer 5 whole and a part of 1st electrode layer 3 may be covered.

[0015]The 1st electrode layer 3 consists of ITO(s) (indium stannic acid ghost), and is formed transparently. As shown in drawing 1 (b), the organic electroluminescence layer 4 comprises four layers, the hole injection layer 4a, the electron hole transporting bed 4b, the luminous layer 4c, and 4 d of electron transport layers, sequentially from the 1st electrode layer 3 side. The hole injection layer 4a is a copper phthalocyanine, the electron hole transporting bed 4b is a triphenylamine derivative, the luminous layer 4c is an aluminum chelate derivative, and 4 d of electron transport layers are formed with lithium fluoride, respectively. The 2nd electrode layer 5 is formed with aluminum (aluminum). The thickness of the 2nd electrode layer 5 of the thickness of the organic electroluminescence layer 4 is usually thinner than the organic electroluminescence layer 4 at about 0.06-0.3 micrometer, and the total value of the thickness of the organic electroluminescence layer 4 and the 2nd electrode layer 5 is 1 micrometer or less at the maximum.

[0016]The protective film 6 is formed by the DLC (diamond like carbon) film containing silicon. 2 - 20at% of the content of silicon is desirable. 50-1000 nm of thickness is preferred.

[0017]Next, the manufacturing method of the organic EL device 1 constituted as mentioned above is explained. The 1st electrode layer 3 which consists of ITO(s) is first formed by sputtering on the glass substrate 2. Next, on the 1st electrode layer 3, laminating formation of the hole injection layer 4a, the electron hole transporting bed 4b, the luminous layer 4c, 4d of electron transport layers, and the 2nd electrode layer 5 is carried out one by one by vacuum evaporation. Next, it transports into the chamber of a plasma CVD device, and without exposing the glass substrate 2 to the atmosphere, by a predetermined film formation condition, a silicon content DLC film is formed so that the 2nd electrode layer 5 and organic electroluminescence layer 4 whole may be covered, and the protective film 6 is

formed. In order to form a silicon content DLC film, membranes are formed where CH_4, $Si(CH_3)_4$, H_2, and Ar gas are put in in the chamber of plasma CVD, for example.

[0018]About the sample of the predetermined size (size of 13 mm x 19 mm of the organic electroluminescence layer 4), gas pressure and the sample which has the protective film 6 of $Si(CH_3)_4$ which changes film formation conditions, such as time, and from which silicon content and thickness differ comparatively were produced. By the samples 1 and 2, 50W was performed for electric power and membranes were formed by 6.7×10^{-1}Pa in gas pressure, and in the samples 3-10, it adjusted suitably and membranes were formed. About each sample, after neglecting it under a room temperature and high-humidity/temperature (60 **, 95%RH), the crack to the protective film 6, the existence of generating of exfoliation, and the existence of growth of a dark spot were investigated. The silicon content of the sample obtained in Table 1 and thickness are shown. After carrying out predetermined time neglect under a room temperature and high-humidity/temperature (60 **, 95%RH) about the sample obtained in Table 2, the result of having investigated the crack to the protective film 6, the existence of generating of exfoliation, and the existence of growth of a dark spot is shown.

[0019]

[Table 1]

	保護膜	
	膜厚 (nm)	Si含有量 (%)
試料1	60	0
試料2	200	0
試料3	200	0.1
試料4	200	60
試料5	200	2
試料6	20	15
試料7	50	15
試料8	200	15
試料9	1000	15
試料10	200	20

[0020]

[Table 2]

	使用試料	クラック、剥離の有無	ダークスポット
実施例1	試料5	高温高湿５００時間後も無し	発生せず
実施例2	試料7	同　上	同　上
実施例3	試料8	同　上	同　上
実施例4	試料9	同　上	同　上
実施例5	試料10	同　上	同　上
比較例1	試料1	有り	室温放置５０時間で発生
比較例2	試料2	初期時に発生	同　上
比較例3	試料3	高温高湿５００時間後発生	高温高湿５００時間後発生
比較例4	試料4	同　上	同　上
比較例5	試料6	同　上	同　上

As shown in Table 1 and 2, in the case of the DLC film which does not contain silicon (comparative examples 1 and 2), even if it changed thickness, a good protective film was not obtained. Also in the case of the DLC film containing silicon, when there was little silicon content (comparative example 3), a crack, exfoliation, and a dark spot occurred after high-humidity/temperature 500-hour neglect. Also when there was much silicon content (comparative example 4), a crack, exfoliation, and a dark spot occurred after high-humidity/temperature 500-hour neglect.

[0021]On the other hand, in Example 1 - Example 5 whose silicon content is 2 - 20at% of a range, in the range whose thickness is 50-1000 nm, neither a crack nor exfoliation occurred and after high-humidity/temperature 500-hour neglect did not generate a dark spot, either. However, as shown in the comparative example 5, when thickness was thinner than the aforementioned range, a crack, exfoliation, and a dark spot occurred after high-humidity/temperature 500-hour neglect.

[0022]When silicon content formed the DLC film of 2 - 20at% of the range as the protective film 6 of the organic electroluminescence layer 4 formed in the flexible substrate, each has followed the flexure deformation of the flexible substrate by the thickness of Examples 1-5, i.e., the range of 50-1000 nm.

[0023]In this embodiment, it has the following effects.

(1) Since neither a crack nor exfoliation occurs even if adhesion is good and thickens thickness as compared with the usual DLC film which does not contain silicon by constituting the protective film 6 from a DLC film containing silicon, the barrier property to the open air containing oxygen and moisture can be improved. Even if it carries out high speed film formation of the thick film, it can control that internal stress becomes large and time for forming the protective film of the thickness which can secure required gas barrier property can be shortened.

[0024](2) By constituting the protective film 6 from a DLC film containing silicon, as compared with the usual DLC film which does not contain silicon, it excels in flexibility, and also when a flexible substrate is used as a substrate, bending of a substrate can be followed.

[0025](3) If thickness is thickened, barrier property will become high, but if it thickens, flexibility will fall. However, in the case of the silicon ** DLC film of this invention, bending of a flexible substrate can be followed by the thickness from which sufficient barrier property is obtained.

[0026](4) The aforementioned effect becomes high when the content of silicon is 2 - 20at%.

(5) When thickness is 1000 nm or less, it can apply to a flexible substrate.

An embodiment may be constituted not only the above but as follows, for example.

[0027]O It may apply to the organic EL device which replaces with the glass substrate 2 and uses a flexible substrate as a substrate.

O Do not necessarily restrict the organic electroluminescence layer 4 to 4 lamination.

[0028]O Don't restrict the material which constitutes each class 4a-4d of the organic electroluminescence layer 4 to the aforementioned composition.

O As a carbon source in plasma CVD method, it may replace with methane and ethane gas and propane may be used.

[0029]O Instead of forming the protective film 6 with the usual plasma CVD method, ECR (Electron Cyclotron Resonance) plasma CVD method may be adopted. In this case, as compared with the usual plasma CVD method, membranes can be formed at low temperature.

[0030]The invention (technical idea) grasped from said embodiment is indicated below.

(1) In the invention according to claim 1 or 2, said protective film is 50-1000 nm in thickness.

[0031](2) Use an ECR plasma CVD method as said plasma CVD method in the invention according to claim 3.

(3) In the invention of a statement, use a tetramethylsilane ($Si(CH_3)_4$) as a source of silicon, and use methane (CH_4) for claim 3 and (2) as a carbon source, respectively.

[0032]

[Effect of the Invention]In order the protective film of claim 1 and the organic EL device of the invention according to claim 2 has the good adhesion over the layer which should be covered with an easy structure as explained in full detail above, and to secure required gas barrier property and endurance, even if it thickens thickness, it has flexibility applicable to a flexible substrate. The invention according to claim 3 is suitable for manufacture of claim 1 and the organic EL device of the invention according to claim 2.

[Translation done.]

* NOTICES *

CLAIMS

[Claim(s)]

[Claim 1]An organic electroluminescence element in which a protective film which consists of a diamond like carbon film which contains silicon on the surface of an organic electroluminescence element was formed.

[Claim 2]said protective film -- silicon -- 2 - 20at% -- the included organic electroluminescence element according to claim 1.

[Claim 3]After laminating the 1st electrode layer, an organic electroluminescence layer, and the 2nd electrode layer on a substrate, so that the whole exposed surface of said organic electroluminescence layer and the 2nd electrode layer may be covered at least, A manufacturing method of an organic electroluminescence element which forms a diamond like carbon film containing silicon with plasma CVD method etc.

[Translation done.]